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14. ABSTRACT Rate constants have been measured for electron attachment to C_5F_5N (297-433 K) and to $2,3,5,6-C_5HF_4N$ (303K) using a flowing-afterglow Langmuir-probe apparatus (at a He gas pressure of 133 Pa). In both cases only the parent anion was formed in the attachment process. The attachment rate constants measured at room temperature are $1.8 \pm 0.5 \times 10^{-7}$ and $7 \pm 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, respectively. Rate constants were also measured for thermal electron detachment from the parent anions of these molecules. For $C_5F_5N^-$ detachment is negligible at room temperature, but increases to $2530 \pm 890 \text{ s}^{-1}$ at 433 K. For $2,3,5,6-C_5HF_4N^-$, the detachment rate at 303 K was $520 \pm 180 \text{ s}^{-1}$. The attachment/detachment equilibrium yielded experimental electron affinities $EA(C_5F_5N) = 0.70 \pm 0.05 \text{ eV}$ and $EA(2,3,5,6-C_5HF_4N) = 0.40 \pm 0.08 \text{ eV}$. Electronic structure calculations were carried out for these molecules and related $C_5H_xF_{5-x}N$ using density-functional theory and the G3(MP2) B3LYP compound method. The EAs are found to decrease by 0.25 eV, on average, with each F substitution by H. The calculated EAs are in good agreement with the present experimental results.					
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Electron attachment and detachment, and the electron affinities of C_5F_5N and C_5HF_4N

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I. OVERVIEW

In recent years we have been studying electron attachment to substituted ring compounds, where, generally speaking, the bonds are strong enough that dissociative electron attachment is unlikely for thermal-energy electrons, and symmetry issues sometimes influence electron detachment from the parent anion (see, for example, Refs. 1–3). In the present experiment we examine substituted pyridines. We have measured rate constants for electron attachment and electron detachment for perfluoropyridine and 2,3,5,6-tetrafluoropyridine:



For simplicity, we will refer to 2,3,5,6- C_5HF_4N as simply C_5HF_4N . Electron affinities (EAs) were determined from the attachment/detachment equilibrium constants. $EA(C_5F_5N)$ has been earlier measured by Dillow and Kebarle, who obtained $0.68 \pm 0.11 \text{ eV}$ from ion equilibrium experiments.⁴ The two molecules differ in that the dipole moment (μ) of C_5F_5N is 0.98 D,⁵ while that of C_5HF_4N has been calculated in the present work to be 2.37 D. The μ of C_5HF_4N is large enough that it may support a weak dipole-bound anion state,⁶ though no such anion state has yet been reported. The role of μ in electron attachment is complicated, but it is not the major factor in determining the magnitude of k_a , excepting the case

where a vibrational Feshbach resonance occurs as a result of a large μ , in a narrow electron energy range below the vibrational excitation threshold.⁷ Other substituted pyridines have large μ (see below), but have negative EAs, which nevertheless can lead to the formation of a metastable anion (as with CO_2 or N_2O).⁷

We have used density-functional and Møller-Plesset perturbation theories to study these and other isomers of C_{2v} symmetry. These other molecules either have an EA too small to study with our apparatus, even negative in most cases, so electron attachment was not attempted for these additional molecules.

II. EXPERIMENT

The present measurements were made in a flowing-afterglow Langmuir-probe (FALP) apparatus. The method⁸ and the Air Force Research Laboratory apparatus⁹ have been well described previously. The attachment/detachment reactions take place in a fast-flowing electron-He⁺, Ar⁺ plasma at 133 Pa of He gas. The C_5F_5N and C_5HF_4N were used as obtained aside from freeze-pump-thaw degassing cycles.¹⁰ Mixtures were prepared at room temperature in He gas of typically 0.3% for C_5F_5N and 6% for C_5HF_4N for accurate measurement of the flow rate of reactant into the FALP. An example of the data obtained in the present work is shown in Fig. 1. The signature of the detachment reaction is apparent in Fig. 1: the initial decay in the electron density is described by the electron attachment rate constant k_a . As time goes on, the competing attachment/detachment processes cause the electron density to reach a steady-state, diffusion-limited

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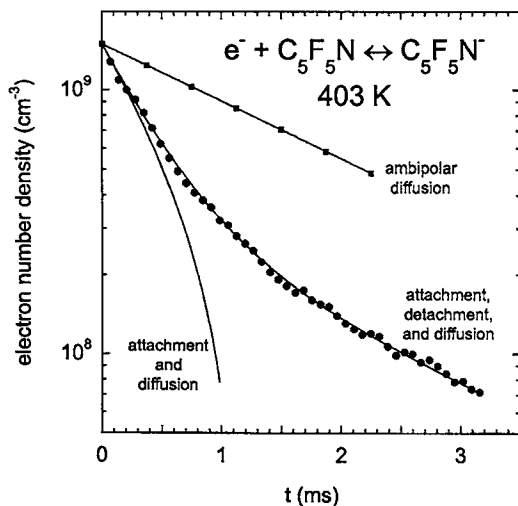


FIG. 1. An example of the electron attachment/detachment data, in 133-Pa He gas at 403 K. The C_5F_5N concentration was $1.37 \times 10^{10} \text{ cm}^{-3}$. The solid lines are solutions of the rate equations governing ambipolar diffusion, electron attachment, and electron detachment. The upper data set was obtained in absence of C_5F_5N and gave the diffusion decay constant ($\nu_D = 500 \text{ s}^{-1}$). The lower data set was fit using $k_a = 1.0 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$ and $k_d = 910 \text{ s}^{-1}$.

condition, provided that the electron detachment rate constant k_d is greater than the ambipolar diffusion decay constant ν_D (otherwise the plasma diffuses away before the steady-state condition is met). The measurement of ν_D was made in absence of reactant gas. The rate constants k_a and k_d were determined from a fit to the data of the solution to the rate equations describing attachment and detachment.¹¹ The k_a are normally estimated accurate to $\pm 30\%$, and the k_d are estimated accurate to $\pm 35\%$. However, in the case of C_5HF_4N , larger uncertainties are estimated because its small k_a , low vapor pressure, and small EA limited the ranges over which data could be obtained.

A mass spectrometer at the downstream end of the flow tube allowed determination of ionic products of the attachment reactions. In the present study, only parent anions were observed from the attachment process.

III. ATTACHMENT AND DETACHMENT RESULTS

The measured k_a and k_d for C_5F_5N are given in Table I for the temperature range of 297–433 K. At 297 K, $k_a = 1.8 \pm 0.5 \times 10^{-7} \text{ cm}^3 \text{ s}^{-1}$. According to the Klotz electron capture theory, this k_a implies attachment upon every 1–2 collisions.¹² The k_a values decline as the temperature increases. The k_d values are immeasurable at 297 K, but climb rapidly to $2530 \pm 890 \text{ s}^{-1}$ at 433 K. The measured k_a and k_d for C_5HF_4N are given in Table II only for the temperature of 303 K because $EA(C_5HF_4N)$ is so low that detachment is significant even at room temperature. Measurements at somewhat higher temperatures would be useful, but the k_a was low enough that a large reactant concentration (n_r) was needed in these measurements—but difficult to sustain in the flow tube given the low vapor pressure of C_5HF_4N . The measured k_a and k_d at 303 K are $7 \pm 3 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ and $520 \pm 180 \text{ s}^{-1}$, respectively. The k_a value implies that electron attachment takes place only once in every 470 collisions, based on the collisional rate constant calculated from the Klotz theory.¹²

IV. ELECTRON AFFINITIES OF C_5F_5N and C_5HF_4N

We have given details of the procedure for deducing EA from the measured k_a and k_d in recent papers.^{2,13} Consideration of the equilibrium constant for attachment/detachment leads to the following relation between k_d and k_a :

TABLE I. Rate constants for electron attachment to C_5F_5N and electron detachment from $C_5F_5N^-$. The experimental uncertainty is $\pm 30\%$ for k_a and $\pm 35\%$ for k_d , except that the k_d in parentheses are not reliable since they are smaller than (or close to) the ambipolar diffusion rate (but give the best fit to the data). For comparison with k_d , the measured ambipolar diffusion decay constant ν_D is given for the electron-(He⁺, Ar⁺) plasma at 133-Pa pressure and $\sim 100\text{-m s}^{-1}$ plasma velocity. The calculated [B3LYP/6-311+G(3df)] entropy S° and integrated specific heat $\int C_p dT$ are given in plain type for C_5F_5N and in italics for $C_5F_5N^-$.

T (K)	S° (meV K ⁻¹)	$\int C_p dT$ (meV)	ν_D (s ⁻¹)	k_a (10 ⁻⁸ cm ³ s ⁻¹)	k_d (s ⁻¹)	EA (eV)
297	338	17.3	(0)	...
	338	18.0	(0)	...
383	4.254	350.4	505	13.2	(612)	(0.68)
	<i>4.498</i>	<i>371.4</i>	505	12.2	(500)	(0.68)
393	4.296	366.1	506	10.2	683	0.69
	<i>4.543</i>	<i>387.9</i>				
403	4.338	382.0	500	10.1	910	0.69
	<i>4.587</i>	<i>404.6</i>	500	9.54	930	0.69
413	4.380	398.1	544	9.55	1490	0.69
	<i>4.631</i>	<i>421.6</i>	544	9.76	1370	0.70
			495	9.97	1330	0.70
423	4.421	414.5	570	10.4	2100	0.70
	<i>4.674</i>	<i>438.7</i>	570	9.56	1930	0.70
433	4.462	431.1	567	9.57	2550	0.71
	<i>4.717</i>	<i>456.1</i>	567	8.50	2500	0.70

TABLE II. Rate constants for electron attachment to 2,3,5,6-C₅HF₄N and electron detachment from 2,3,5,6-C₅HF₄N[−]. The experimental uncertainties are ±45% and ±35% for k_a and k_d , respectively. For comparison with k_d , the measured ambipolar diffusion decay constant ν_D is given for the electron-(He⁺, Ar⁺) plasma at 133-Pa pressure and ~100-m s^{−1} plasma velocity. The calculated [B3LYP/6-311++G(3df,2p)] entropy S° and integrated specific heat $\int C_p dT$ are given in plain type for 2,3,5,6-C₅HF₄N and in italics for 2,3,5,6-C₅HF₄N[−].

T (K)	ν_D (s ^{−1})	S° (meV K ^{−1})	$\int C_p dT$ (meV)	k_a (10 ^{−10} cm ³ s ^{−1})	k_d (s ^{−1})	EA (eV)
303	351	3.698	208.6	8.5	520	0.40
	332	<i>3.942</i>	228.2	5.0	580	0.39
	324			8.0	480	0.40
	324			6.5	505	0.40

$$k_d = k_a L_0 (273.15/T) \exp[-(EA/kT) - (\Delta S^\circ/k) - (H_T - H_0)/kT]. \quad (3)$$

In Eq. (3), k is Boltzmann's constant, L_0 is Loschmidt's number, EA is the electron affinity (at 0 K, by definition), ΔS° is the entropy change due to electron attachment at temperature T , and $H_T - H_0$ is a thermal-energy correction. The entropy change was calculated for each T , as laid out in Sec. V, below, allowing the detachment energy to be determined at temperature T . The integrated heat capacities contained in $(H_T - H_0)$ then allow this energy to be reduced to the EA (at 0 K, by definition). The calculated entropies and heat capacities for the neutrals and anions are tabulated in Tables I and II for each relevant temperature, along with the apparent EA deduced from each datum, using Eq. (3). In earlier work we have shown that the calculated quantities are accurate within a few percent.¹³ Since the calculated quantities contribute only 7%–8% of the EA value, they contribute negligibly to the uncertainty in EA. Entropies for the electron were taken from the JANAF tables.¹⁴

EA(C₅F₅N) was found to be 0.70±0.05 eV from the present data, in excellent agreement with the measurement of Dillow and Kebab, who obtained 0.68±0.11 eV.⁴ EA(C₅HF₄N) was found to be 0.40±0.08 eV. The uncertainty in EA(C₅HF₄N) is larger than in EA(C₅F₅N) because C₅HF₄N could only be studied at one temperature (303 K), as a result of its low EA, low k_a , and low vapor pressure.

The calculated entropy results are interesting to compare: $T\Delta S^\circ$ is negative for the C₅F₅N attachment process, but positive for the C₅HF₄N case. The entropy term arises from

$$S^\circ = S_a^\circ - S_n^\circ - S_e, \quad (4)$$

where the subscripts a , n , and e refer to the anion, neutral, and electron. For C₅F₅N, the usual situation was found, namely, that electron attachment is accompanied by a decrease in entropy (e.g., $T\Delta S^\circ = -15$ meV at 413 K). For C₅HF₄N, $S_a^\circ - S_n^\circ$ is of similar (positive) size as with the C₅F₅N case, but S_e° is smaller due to the lower temperature for which detachment took place, making $T\Delta S^\circ$ positive overall, namely, +7 meV at 303 K. (The temperatures chosen in these examples are those at which the attachment frequency, $k_a n_e$, was comparable to the detachment frequency, k_d .) The positive $T\Delta S^\circ$ term for C₅HF₄N inhibits electron detachment, as is evident from Eq. (3).

V. COMPUTATIONAL METHOD AND RESULTS

Two types of calculations were carried out in this work using the GAUSSIAN-03 set of programs.¹⁵ Density-functional theory (DFT) based on the hybrid functional B3LYP,^{16,17} with a large basis set [6-311++G(3df,2p)],¹⁸ was applied to determine the integrated heat capacities and entropies needed to interpret the experimental results on C₅F₅N and C₅HF₄N in terms of EAs. Calculations were also carried out using the compound method G3(MP2)//B3LYP in order to get an accurate theoretical EA.^{19,20} This latter method utilizes the hybrid functional B3LYP with a smaller basis set [6-31G(d)] to determine the molecular geometries and zero-point energies (ZPEs) of the neutral and anion, and applies Møller-Plesset perturbation theory to determine a high-level energy for those geometries. The G3(MP2)//B3LYP method has been shown accurate *on average* to ±54 meV for ionization potentials and electron affinities.¹⁹ The results of the calculations are given in Tables I and II (integrated heat capacities and entropies) and in Table III (ZPEs, total energies, EAs, μ). In two cases noted in Table III, namely, 2,6-C₅H₃F₂N[−] and C₅H₅N[−], the small basis set used with the G3(MP2)//B3LYP compound method yielded C_s symmetry, while the larger basis set used with the “pure” DFT method in Table III yields a planar C_{2v} symmetry. MP2 optimizations likewise gave C_s for the small basis set, for both anions. MP2 optimization with the large basis set remained at C_s symmetry for C₅H₃F₂N[−], but went to C_{2v} for C₅H₅N[−]. Thus, it is virtually certain that C_{2v} symmetry is correct for C₅H₅N[−], but it is uncertain whether C₅H₃F₂N[−] is C_s or C_{2v}.

Optimized geometries for C₅F₅N and C₅HF₄N neutrals and anions are shown in Figs. 2 and 3. The geometry change in going from the neutral to the anion appears similar for these two molecules. The main difference is in the effect of electron attachment on the F or H atom bound to C4, both in the C–F versus C–H bond length change as well as in the out-of-plane angle. Natural population analysis²¹ (NPA) indicates that the “extra” electronic charge in the anion is stabilized through delocalization around the ring (0.62e for C₅F₅N[−] and 0.70e for C₅HF₄N[−]) and on the fluorine atoms (0.38e for C₅F₅N[−] and 0.24e for C₅HF₄N[−]). In a related computational study, Alkorta *et al.*²² found that small anions will associate with perfluoropyridine, binding closer to C4 than N. Their results are also consistent with our NPA analysis which yielded 64% of the extra charge in C₅F₅N[−] found

TABLE III. Results of Møller-Plesset and density-functional calculations for $C_5H_xF_yN$ neutrals and anions. Energies are in hartree, except for EAs.

System	G3(MP2)//B3LYP ^a	Pure DFT ^b
C_5F_5N (C_{2v} , 1A_1)		
ZPE	0.046 38	0.048 08
total energy (0 K)	-743.681 14	-744.674 80
EA (eV)	0.645	0.800
dipole moment (<i>D</i>)	0.93 ^c	1.01 (0.98±0.08) ^d
$C_5F_5N^-$ (C_s , $^2A'$)		
ZPE	0.042 96	0.044 24
total energy	-743.704 86	-744.704 19
2,3,5,6- C_5HF_4N (C_{2v} , 1A_1)		
ZPE	0.054 22	0.055 80
total energy (0 K)	-644.530 54	-645.406 42
EA (eV)	0.272	0.380
dipole moment (<i>D</i>)	2.61 ^c	2.37
2,3,5,6- $C_5HF_4N^-$ (C_s , $^2A'$)		
ZPE	0.050 05	0.051 35
total energy (0 K)	-644.540 52	-645.420 40
3,4,5- $C_5H_2F_3N$ (C_{2v} , 1A_1)		
ZPE	0.061 98	0.063 74
total energy (0 K)	-545.353 58	-546.110 95
EA (eV)	0.138	0.288
dipole moment (<i>D</i>)	0.88 ^c	0.51
3,4,5- $C_5H_2F_3N^-$ (C_s , $^2A'$)		
ZPE	0.058 34	0.059 74
total energy (0 K)	-545.358 64	-546.121 54
2,4,6- $C_5H_2F_3N$ (C_{2v} , 1A_1)		
ZPE	0.062 15	0.063 79
total energy (0 K)	-545.385 45	-546.142 96
EA (eV)	-0.058	0.056
dipole moment (<i>D</i>)	2.48 ^c	2.34
2,4,6- $C_5H_2F_3N^-$ (C_s , $^2A'$)		
ZPE	0.058 31	0.059 79
total energy (0 K)	-545.383 32	-546.145 02
2,6- $C_5H_3F_2N$ (C_{2v} , 1A_1)		
ZPE	0.070 02	0.071 83
total energy (0 K)	-446.222 36	-446.861 65
EA (eV)	-0.213	-0.089
dipole moment (<i>D</i>)	4.22 ^c	3.85
2,6- $C_5H_3F_2N^-$		
ZPE ^c	0.064 92	0.064 82
total energy (0 K) ^c	-446.214 53	-446.858 37
4- C_5H_4FN (C_{2v} , 1A_1)		
ZPE	0.077 70	0.079 60
total energy (0 K)	-347.044 04	-347.565 17
EA (eV)	-0.630	-0.453
dipole moment (<i>D</i>)	0.61 ^c	0.73
4- $C_5H_4FN^-$ (C_1 , 2A)		
ZPE	0.070 61	0.076 19
total energy (0 K)	-347.020 89	-347.548 51
C_5H_5N (C_{2v} , 1A_1)		
ZPE	0.085 49	0.087 53
total energy (0 K)	-247.878 76	-248.281 73
EA (eV)	-0.549	-0.543
dipole moment (<i>D</i>)	2.36 ^c	2.27 (2.215±0.010) ^d
$C_5H_5N^-$		
ZPE ^c	0.07892	0.08127
total energy (0 K) ^c	-247.858 58	-248.261 77

^aCompound method with G3(MP2) energy calculated for a DFT [B3LYP/6-31G(*d*)] geometry and ZPE (Ref. 19).

^bB3LYP/6-311++G(3*df*,2*p*)/B3LYP/6-311++G(3*df*,2*p*) plus ZPE.

^cThe dipole moment was taken from the QCISD(T)/6-31G(*d*) step of the G3(MP2)//B3LYP compound method.

^dExperimental dipole moments were taken from Ref. 5.

^eThe point group and state are (C_s , $^2A'$) for the B3LYP/6-31G(*d*) geometry in the G3(MP2)//B3LYP method, and (C_{2v} , 2B_1) for the larger basis set [6-311++G(3*df*,2*p*)] used in the "pure" DFT method; see text.

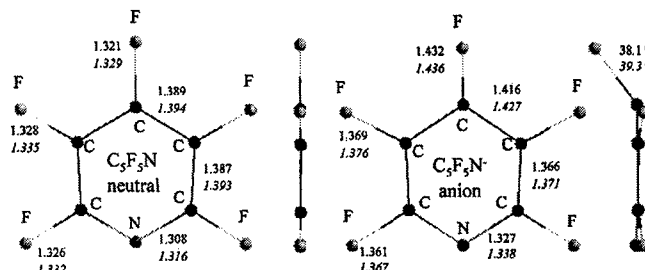


FIG. 2. Calculated structures for C_5F_5N (C_{2v}) and $C_5F_5N^-$ (C_s), with views above and to the side of the average plane of the ring. The bond lengths in plain type are from B3LYP/6-311++G(3*df*) optimizations. Those in italics are the B3LYP/6-31G(*d*) optimizations used in the G3(MP2)//B3LYP calculations. The angle shown is $180^\circ - \angle N1-C4-F$.

in the C3–C5 half of the molecule (53% in the $C_5HF_4N^-$ case). A similar change in neutral-to-anion geometry was found for the $C_5H_2F_3N$ isomers, but the pyridine anion and related C_5H_4FN and $C_5H_3F_2N$ anions are nearly planar, presumably because of the inability of the hydrogen atoms to accommodate the extra charge.

The question naturally arises as to why the attachment rate constants for C_5F_5N and C_5HF_4N are so different. Both reactions are exothermic and the geometry changes upon attachment of an electron to the neutral molecules are similar. However, the magnitude of the energy gained upon attachment is different, reflecting the different stabilities of the negative ions. The answer may lie in the kind of analysis carried out by Gallup *et al.* for dissociative electron attachment, where a strong correlation between the vertical electron attachment energy and the thermal rate constant for attachment was found.²³

We also calculated total energies for the rest of the $C_5H_xF_{5-x}N$ series with C_{2v} symmetry. These results are included in Table III along with EAs and dipole moments. Experimental studies of electron attachment were not attempted for the commercially available species 2,6- $C_5H_3F_2N$ and C_5H_5N because the calculated electron affinities are negative, as one would guess from the trend found in going from C_5F_5N (EA=0.70 eV) to C_5HF_4N (EA=0.40 eV). The experimental and G3(MP2)//B3LYP calculated electron affinities are plotted in Fig. 4. A fit to the calculated values shows an average of 0.25 eV decrease in EA per H-atom substitution. The individual calculated EAs are more accurate than the average values along the fitted

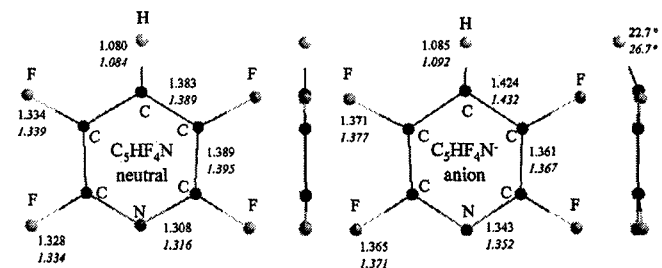


FIG. 3. Calculated structures for 2,3,5,6- C_5HF_4N (C_{2v}) and 2,3,5,6- $C_5HF_4N^-$ (C_s), with views above and to the side of the average plane of the ring. The labeling is the same as in Fig. 2, except for the H atom: the angle shown is $180^\circ - \angle N1-C4-H$.

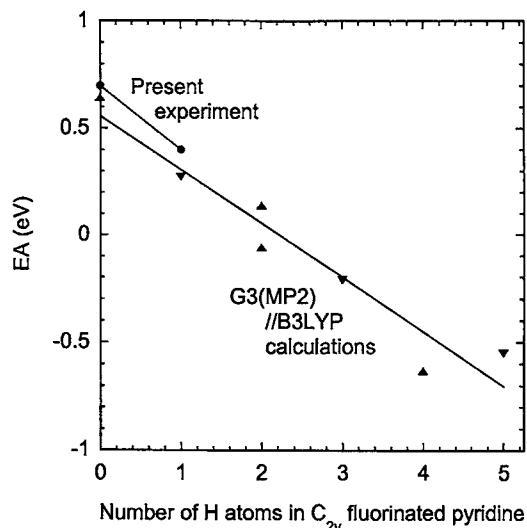


FIG. 4. Variation of EA with the number of H atoms in C_{2v} fluorinated pyridine. The line through the calculated EAs indicates an average decrease in EA of 0.25 eV per H-atom substitution (but the individual points are more accurate than the average). The upward-pointing triangles are for molecules with a F atom bound to C4 (opposite the N atom in the ring). The downward-pointing triangles are for molecules with a H atom bound to C4. The EA values are from Table III.

line. It is worthy of note that while the calculations show that EA(2,6- $C_5H_3F_2N$) is negative, the calculated dipole moment of 2,6- $C_5H_3F_2N$ is large enough to support a dipole-bound anion state of about 11-meV electron binding energy.²⁴ The calculated dipole moments in three cases (2,3,5,6- C_5HF_4N , 2,4,6- $C_5H_2F_3N$, and C_5H_5N) are marginal for supporting a dipole-bound state, with electron binding energies predicted to be sub-meV.²⁴

VI. CONCLUSIONS

Rate constants were measured for electron attachment to C_5F_5N (297–433 K) and to C_5HF_4N (303 K), using a flowing-afterglow Langmuir-probe apparatus, in a helium bath at 133-Pa pressure. Attachment was found to form only the parent anions at the temperatures studied. C_5HF_4N attaches electrons at a rate that is 260 times smaller than for C_5F_5N , at room temperature. Rate constants were also measured for thermal electron detachment from the parent anions. Coupling these measurements with entropies and integrated heat capacities obtained from the DFT calculations, we obtained $EA(C_5F_5N) = 0.70 \pm 0.05$ eV and $EA(C_5HF_4N) = 0.40 \pm 0.08$ eV. Calculations were carried out on these molecules and other fluorinated pyridines using DFT and the G3(MP2)//B3LYP compound method. The calculated EAs are in good agreement with the experimental results.

The present $EA(C_5F_5N)$ is in excellent agreement with that of Dillow and Kebarle (0.68 ± 0.11 eV).⁴ We note that we have now studied a number of molecules for which EAs have been earlier measured at the University of Alberta, and have found agreement well inside the stated uncertainties, in all cases.

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